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Improving the flexibility and compostability of starch/poly(butylene cyclohexanedicarboxylate)-based blends

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Abstract

Fully biobased blends of thermoplastic starch and a poly(butylene cyclohexanedicarboxylate)-based random copolyester containing 25% of adipic acid co-units (PBCEA) are prepared by melt blending and direct extrusion film casting. The obtained films are characterized from the physicochemical and mechanical point of view and their fragmentation under composting conditions is evaluated. The results demonstrate that the introduction of adipic acid co-units in the PBCE macromolecular chains permits to decrease the blending temperature, thus avoiding unwanted starch degradation reactions. Moreover, the presence of small amounts of citric acid as compatibilizer further improves the interfacial adhesion between the two components and promotes the formation of micro-porosities within the films. The synergistic combination of these factors leads to the development of materials showing an elastomeric behavior, i.e. no evident yield and elongation at break higher than 450%, good moisture resistance and fast fragmentation in compost.

Keywords

Thermoplastic starch (TPS), poly(butylene cyclohexanedicarboxylate), compatibilization, biobased polymer blends, elastomeric behavior

1. Introduction

The growing environmental concern about (micro)plastic pollution even in remote regions of our planet is posing great attention on the urgent need of reducing the employment of long-lasting polymeric materials. Especially for the fabrication of disposable items, where indefinite in-service durability is not required, biodegradable plastics may represent a solution.(Kabir et al., 2020) The combination of biodegradability and biobased character is even more desirable, as it would permit to limit the dependence on fossil resources and facilitate the transition towards a circular economy. In the last decades, many biopolymers have attracted considerable interest and have been studied for the production of sustainable formulations with comparable (or superior) technical performances and competitive costs with respect to traditional materials.(RameshKumar et al., 2020; Yin & Yang, 2020) Among various possibilities, starch has been widely used due to its low cost and high abundance.(Ojogbo et al., 2020) It is in fact produced by many plants and stored in the cells as source of energy.(H. Liu et al., 2009) However, due to strong intermolecular interactions, starch in its native form is not thermoplastic. Therefore, it must be processed, through the joint action of plasticizers such as glycerol and water, heat and shear stress, into a workable plastic material.(Khan et al., 2017) If, in principle, 100% thermoplastic starch (TPS) films can be produced, some important drawbacks, i.e. moisture sensitivity, which causes starch recrystallization, and poor mechanical properties, hamper their applicability.(Ojogbo et al., 2020) In the attempt of better exploiting the favorable characteristics of starch, TPS has been blended, most commonly via melt blending, with a wide range of polymers. Studies include oil-derived commodities and greener alternatives, being aliphatic and aliphatic/aromatic polyesters the most explored options.(Kaseem et al., 2012) In particular, much research has focused on commercially available (co)polyesters like polylactic acid,(Zaaba & Ismail, 2019) polyhydroxyalcanoates,(Parulekar & Mohanty, 2007) polycaprolactone,(Bulatović et al., 2019; Ortega-Toro et al., 2016) poly(butylene succinate),(Lai et al., 2005) and poly(butylene adipate-*co*-terephthalate).(Ivanič et al., 2019; Wang et al., 2015; Wei et al., 2015)

Aiming at obtaining TPS-rich blends with high flexibility and low retrogradation issues, in this contribution another approach, that deviates from the commonly adopted strategies, has been chosen. Instead of employing existing polymeric matrices and then working on the compatibilization between the blend components by further chemical modification of the polymer or by adding significant amounts of other compounds that act as compatibilizers, a tailor-made polyester, i.e. a poly(butylene cyclohexanedicarboxylate-*co*-adipate) copolymer (PBCEA), has been synthesized to achieve the desired properties.

The two acid subunits, their molar ratio and the polymer architecture have been specifically selected for the following reasons. On the one hand, poly(butylene cyclohexanedicarboxylate) (PBCE) is

characterized by the presence of a cycloaliphatic ring in the repeating unit, whose structure resembles the glucose molecule and may thus improve the compatibility with starch. This polyester displays high melting temperature and good resistance to heat, light and moisture, making it very appealing for uses as packaging material.(Gigli et al., 2013; Gigli, Lotti, et al., 2014) Additionally, both monomers leading to PBCE can be obtained from renewable resources, i.e. from succinic acid and limonene-derived terephthalic acid.(Genovese et al., 2016) On the other hand, adipic acid, it too potentially biobased,(Skoog et al., 2018) has been randomly introduced along the PBCE main chain with the aim of lowering the melting of the crystalline domains. This way the blending temperature can be decreased, thus avoiding any undesired starch degradation through the combined action of heat and shear stress, with a consequent decline of its properties.(W.-C. Liu et al., 2010)

To further increase the miscibility between the blend components, low amounts of citric acid (CA) have been added to the formulation, as CA promotes the fragmentation and dissolution of starch granules by crosslinking, (trans)esterification and hydrolysis reactions during melt compounding.(Carvalho et al., 2005; Ghanbarzadeh et al., 2011; Shi et al., 2007)

Films with a fixed 50:50 composition between PBCEA and TPS and different amount of CA have been prepared by melt blending and direct film casting, and subsequently characterized from the molecular, morphological, thermal and mechanical point of view. Surface wettability and moisture absorption have been also investigated. Lastly, end-of-life fate of the developed materials has been evaluated by lab-scale composting studies over 4-weeks period.

2. Materials and methods

2.1 Materials

Trans-cyclohexane-1,4-dicarboxylic acid (CHDA, 98%) and adipic acid (AA, 99%) were purchased from TCI Chemicals (Tokyo, Japan), glycerol (99%) from Alfa Aesar (Haverhill, MA, USA), while wheat starch (WS), 1,4-butanediol (BD, 99%), citric acid (CA, 99.5%) and titanium tetrabutoxide (TBT, 97%) from Sigma-Aldrich (Milan, Italy). TBT was distilled before use, while all the other compounds were used as received.

2.2 Polymer synthesis and starch plasticization

PBCEA was synthesized through two-step melt polycondensation. CHDA, AA and BD in molar ratio 0.75:0.25:1.4 were added to a 200 mL glass reactor together with the catalyst (TBT, 100 ppm/g of polymer) and 0.1% wt. of glycerol (with respect to theoretical polymer mass). The reaction mixture, kept under nitrogen atmosphere, was heated to 180°C in a thermostated salt-based bath and allowed to proceed until more than 90% of the theoretical water distilled off. In the second step, the pressure

was gradually reduced to 0.1 mbar and the temperature increased to 240°C. The polymerization was stopped when the torque, continuously recorded during the reaction, reached a constant value.

Wheat starch plasticization was performed as previously described.(Genovese et al., 2018) Briefly, 72% wt. of wheat starch was mixed in a co-rotating twin screw extruder (DSM Explorer 5&15 CC Micro Compounder) with 28% wt. of glycerol for 3 min at 30 rpm, with a temperature profile of 135-140-145°C. The obtained TPS filament was pelletized to be used for blend preparation.

2.3 Blend processing and filming procedure

PBCEA and TPS were separately pelletized and dried under vacuum at 50 °C for 24 h. Three blend formulations, in addition to pristine PBCEA, were developed (**Table 1**). A polymer ratio equal to 50% wt. of PBCEA was selected based on previous results and different concentrations of CA (0.5 and 1.0% wt.) as compatibilizer have been tested.(Genovese et al., 2018)

The microextruder was used in speed control mode at 50 rpm to achieve the melt blending of PBCEA and TPS. PBCEA was first introduced in the compounder, while TPS was added after 2 mins. Mixing was then continued for 1 additional minute. The temperature profile in the three zones of the extruder was set to 150-155-165°C to obtain adequate conditions for subsequent direct filming. For this last step, the compounder was switched in force control mode, and a microfilm die coupled with a casting film line (DSM Film Device) was added. The processing parameters to produce cast films were modified according to the rheological behavior of the blends, as reported in **Table 1**, under constant speed (500 mm min^{-1}) and torque (40 Nmm). Films of about 100-120 µm thickness were obtained.

Table 1. Formulations and film processing parameters of PBCEA/TPS blends

Sample	PBCEA (% wt.)	TPS (% wt.)	CA (% wt.)	Force (N)
PBCEA	100	0	0	650
PBCEA/TPS	50	50	0	750
PBCEA/TPS-CA0.5	50	49.5	0.5	800
PBCEA/TPS-CA1	50	49	1	850

2.4 Physicochemical characterization

PBCEA composition was verified by ^{1}H-NMR on a Varian INOVA 400 MHz instrument (Agilent Technologies). Chloroform-d containing 0.03% (v/v) tetramethylsilane as internal standard was used as solvent with a polymer concentration of about 0.5 %wt. Spectra were collected at RT. The molecular weight and dispersity index (DI) were obtained by gel permeation chromatography (GPC) by employing a 1100 Hewlett Packard system (Agilent Technologies) equipped with a PLgel 5 mm MiniMIX-C column and a refractive index detector. Chloroform was used as eluent with a 0.3 mLmin-

^{1} flow. Polystyrene standards in the molecular weight range 4k-200k were used to build the calibration curve.

Surface morphology and cross-section were studied on a field emission scanning electron microscope (FE-SEM, SUPRA™ 35, Carl Zeiss SMT) on gold sputtered samples.

For cross-section analysis specimens were freeze-cut in liquid nitrogen along the transverse direction.

A Jasco FT-IR 615 spectrometer equipped with a Germanium crystal and operating in attenuated total reflection (ATR) mode was employed for infrared (IR) spectrum measurements in the 400-4000 cm^{-1} range.

Thermogravimetry (TGA) was carried out under nitrogen atmosphere (30 $mLmin^{-1}$) on a Perkin Elmer TGA7 apparatus. A heating scan of 10 $°Cmin^{-1}$was used for the analysis.

Calorimetric analysis was run on a Perkin Elmer DSC6 instrument. Weighed samples were encapsulated in aluminum pans and heated to 180°C. After holding at this temperature for 3 min to delete any thermal history, specimens were quenched to -60 °C and then heated at 20 $°Cmin^{-1}$ up to 160°C (II scan). To determine the crystallization rate under non-isothermal conditions, samples were cooled from the melt (see above) at 5 $°Cmin^{-1}$.

Static water contact angle (WCA) was measured on blend films at room temperature (RT) by using a KSV CAM101 instrument. Side profiles of deionized water drops were recorded for image analysis after 2 s from deposition. Contact angles are reported as the average value of at least ten different measurements.

The moisture content (MC) was evaluated at 25 °C and 53% of relative humidity (RH). Measurements were taken after 1 and 5 weeks of incubation. The test was run in triplicate, according to the following procedure: samples measuring 20 × 20 mm were cut and pre-dried under vacuum at 40 °C for 72 h. The films were then placed in desiccators containing $Mg(NO_3)_2$ till constant weight was detected. MC was estimated according to Eq. 1:

$$MC(\%) = \frac{W_{Final} - W_{Initial}}{W_{Final}} \times 100 \qquad \text{(Eq. 1)}$$

where W_{Final} is the weight of sample after 1 or 5 weeks at 53% RH and 25 °C and $W_{Initial}$ is the weight of pre-dried samples.

2.5 Mechanical characterization

Tensile tests were performed on films by employing an Instron 4465 testing machine, equipped with a rubber grip and a 100 N load cell. A preload of 1 MPa and a crosshead speed of 10 $mm\ min^{-1}$ were applied. Results are provided as average ± standard deviation of at least 5 replicates.

2.6. Composting

Composting tests were carried out at (58.0 ± 0.1)°C using mature compost supplied by HerAmbiente S.p.A. (Bologna, Italy) and having the following composition (as declared by HerAmbiente): organic

carbon: 22.08% of the dry solid, humic and fulvic carbon: 13.44% of the dry solid, C/N ratio: 12.97, pH: 8.15 and salinity: 2.88 dS m^{-1}. Each sample (about 20 × 20 mm in size) was placed in a 100 mL glass bottle in between two layers of compost (20 g each). 10 mL of deionized water was added. Specimens were recovered at determined time intervals, washed accordingly to the procedure previously described,(Genovese et al., 2014) and dried over P_2O_5 under vacuum to constant weight. Weight loss was calculated as follows:

$$((m_i - m_f) / m_i) \times 100 \qquad \text{(Eq. 2)}$$

where m_f and m_i are the final and the initial sample weight, respectively.

3. Results and Discussion

High molecular weight PBCEA (M_n = 37.5 kDa, DI = 2.1), whose chemical structure was elucidated by ^{1}H-NMR analysis (**Figure 1**), was obtained.

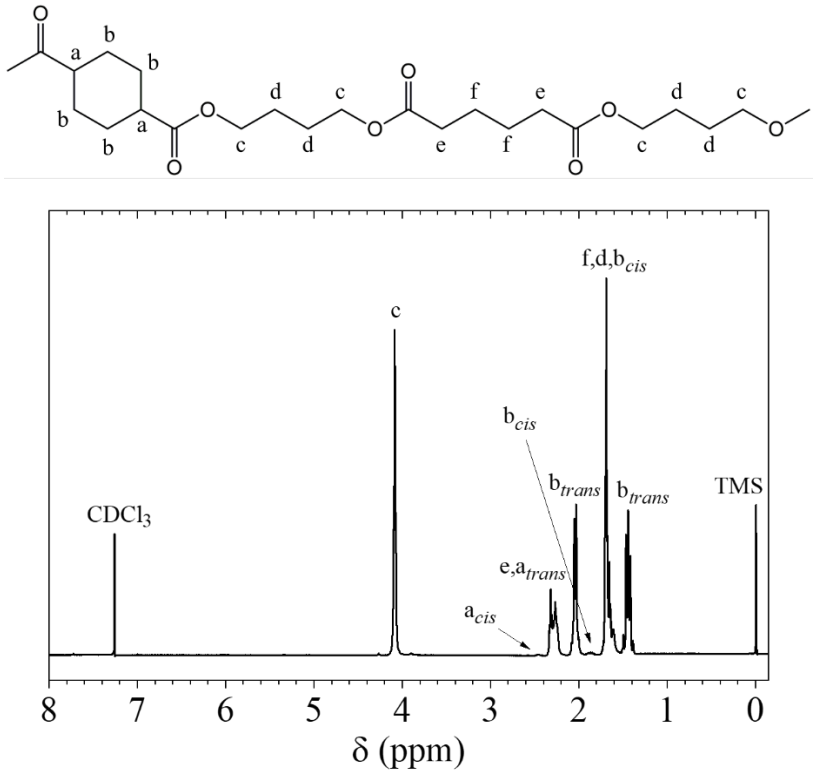

Figure 1. ^{1}H-NMR spectrum of PBCEA with resonance assignments.

The copolymer composition, deduced from the integration of the peaks located at 2.27 ppm (e), 2.31 ppm (a_{trans}) and 2.46 ppm (a_{cis}) resulted close to the feed (27.8 mol% of butylene adipate co-units). Furthermore, the calculation of the ratio between the area of the b_{cis} (1.87 ppm) and b_{trans} (2.04 ppm) peaks evidenced that no significant isomerization occurred during the reaction as the measured content of *cis* isomer was equal to 2.7%. These results demonstrated that the adopted polymerisation protocol was optimized with respect to previously reported conditions.(F. Liu et al., 2016)

All materials were then easily processed into blends and allowed for the production of films suitable for subsequent characterization. To obtain films of comparable thickness, the counter thrust parameter (Force, **Table 1**) was optimized for each formulation during the film casting, since the presence of CA, due to its crosslinking action,(Ghanbarzadeh et al., 2011; Shi et al., 2007) caused an increase in resistance forces. Defect-free films of variable thickness in the range 30-100 μm (modulated based on the subsequent characterization technique) have been obtained. Their light colour (**Figure 2A**) indicates the absence of undesired degradation reactions, e.g. caramelization, during processing.

Figure 2B reports the micrographs of the fracture surfaces for PBCEA and PBCEA/TPS blend films. The cross section of the neat polyester film displays a uniform phase with a few submicrometric cavities, which can be due to the evaporation of low molecular weight residues from the synthesis step. As to the PBCEA/TPS blend, a better dispersion between the two phases with respect to other PBCE-based blends of similar composition previously investigated can be observed.(Genovese et al., 2018) However, phase separation highlighted by the presence of some cracks and detachments, is still present. The addition of CA during compounding improves interface adhesion. Indeed, numerous trabecular connections are identified between the two polymers. On the other hand, the concentration and size of the cavities rise, probably because of degradation and (trans)esterification reactions occurring during reactive extrusion in the presence of CA.(Olivato et al., 2014)

A further increase of the CA content makes the above described phenomena more evident. Indeed, a better binding of the two phases is reached, but an increment of the number of voids, which are mainly located in the PBCEA phase, can be concomitantly observed. Therefore, the morphological analysis suggests that CA, during the reactive extrusion, exerts a double function.

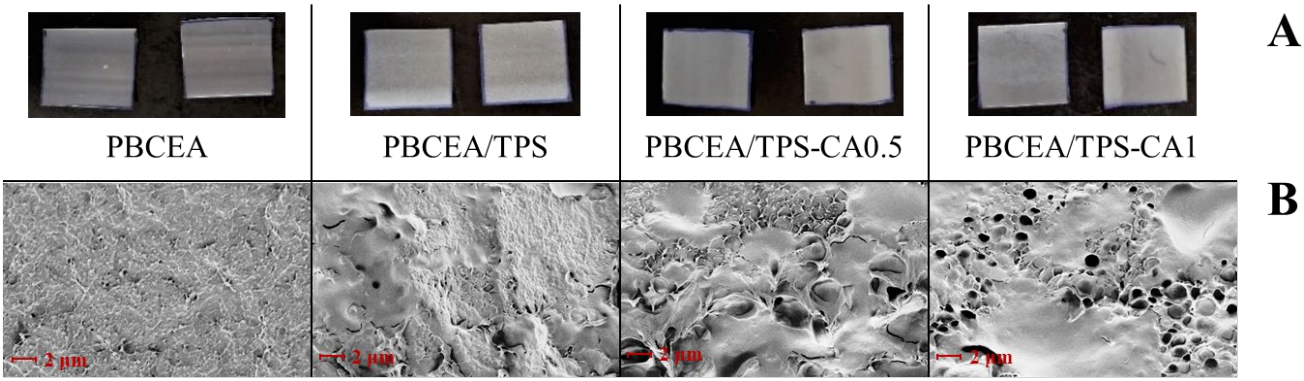

Figure 2. A) Photographs of PBCEA and PBCEA/TPS films. Squares of about 9 cm^2 are depicted. B) FESEM micrographs of the cross sections of PBCEA and PBCEA/TPS blends.

On the one hand, owing to crosslinking and (trans)esterification reactions, it acts as compatibilizer and plasticizer, thus improving the mixing and adhesion of the blend components. On the other hand,

the hydrolysis reactions produce volatiles responsible for the formation of porosities within the films.(Carvalho et al., 2005)

To verify the occurrence of interactions among the blend components, ATR-FTIR analyses were performed. The full infrared spectra (3750–750 cm^{-1}) of PBCEA, TPS and PBCEA/TPS blends are collected in **Figure 3A**. In the blends, the absorption bands corresponding to the functional groups of both main components are clearly visible, indicating that their chemical stability was not influenced by the extrusion and filming treatment. A broad peak, typical of OH stretching vibration of inter- and intra-molecular bonding of hydroxyl groups, is present at about 3350 cm^{-1} (**Figure 3B**).

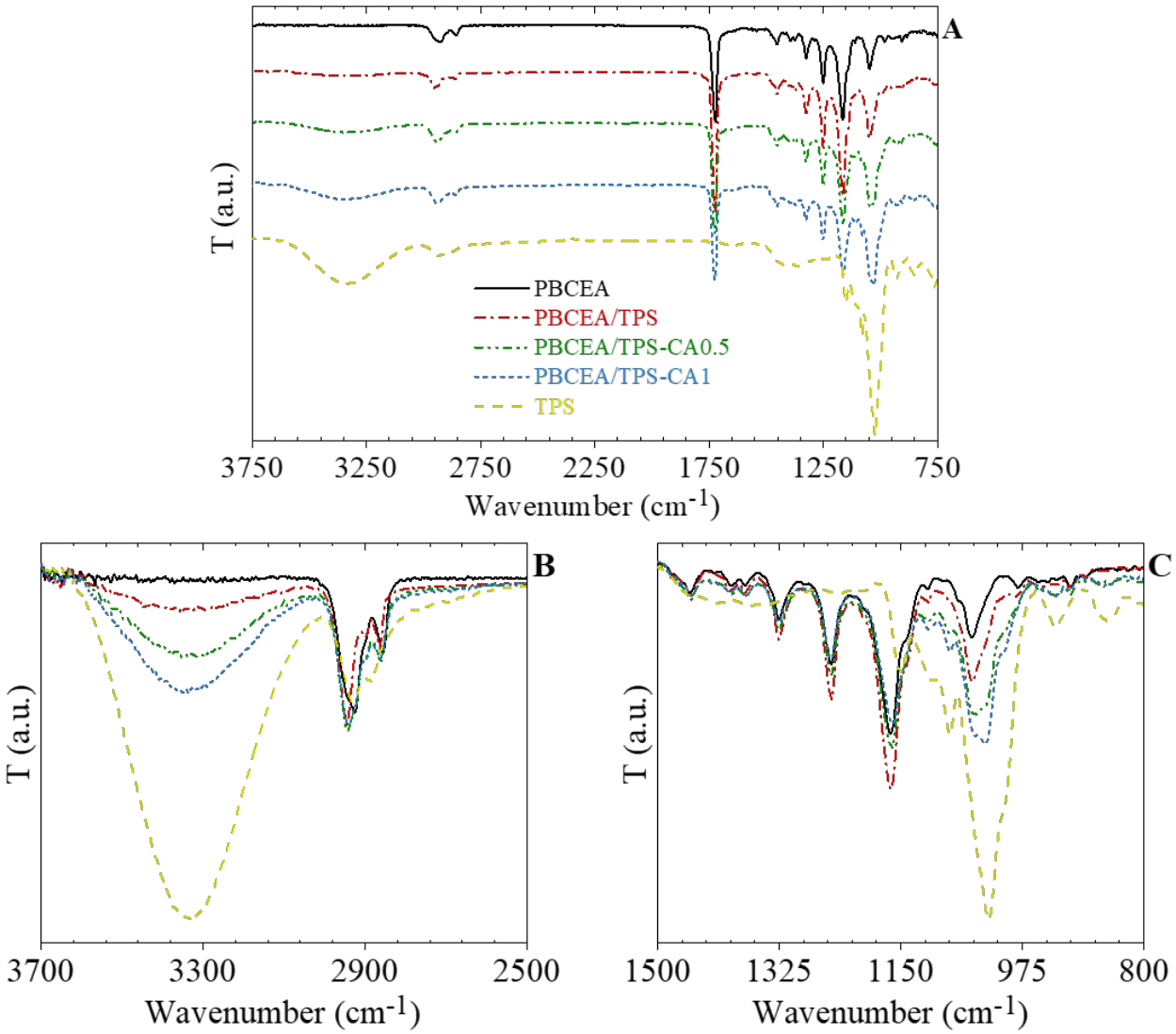

Figure 3. ATR-FTIR spectra of PBCEA, TPS and PBCEA/TPS blends: A) full spectrum, B) enlargement of the 3700 – 2500 cm^{-1}region and C) enlargement of the 1500 – 800 cm^{-1}region.

Its intensity depends on the samples' chemical composition. Specifically, the magnitude of the OH band for the PBCEA/TPS blends is within those of PBCEA (very low), and TPS (more intense). Further, higher concentrations of CA are shown to enhance this value.

All samples display aliphatic asymmetrical and symmetrical stretching C-H vibration peaks in the 2840 – 3000 cm^{-1} region, although some differences can be evidenced. Specifically, with respect to PBCEA, PBCEA/TPS blends display one additional small peak located at 2900 cm^{-1}, assigned to C-H stretches of glycerol, and a shift of the more intense peak from 2923 cm^{-1} to 2943 cm^{-1}, due to the heterocyclic rings of starch.(Hablot et al., 2013) In addition, in the CA-containing blends, a shoulder at 2923 cm^{-1} can be observed, suggesting a better interaction among the blend components. The peak centered at 1721 cm^{-1}, relative to the carbonyl C=O stretching vibration of the PBCEA ester groups, is not significantly affected by the blending process. The fingerprint region (800 – 1500 cm^{-1}, **Figure 3C**) contains useful information on the crystalline and amorphous regions in starch-based samples, respectively assigned to the bands located at 1047 and 1022 cm^{-1}.(Capron et al., 2007; Genovese et al., 2018)

While PBCEA and PBCEA/TPS samples were characterized by a major adsorption band at about 1047 cm^{-1}, the peak at 1022 cm^{-1} is more marked in CA-containing blends, demonstrating an inversely proportional behavior of the TPS degree of crystallinity with the CA content, as already reported.(Genovese et al., 2018) Lastly, also the signal at 1000 cm^{-1}, relative to starch/water interactions, is more intense,(Capron et al., 2007) indicating that CA presence enhances the samples' water content.

To better analyse the behaviour of different blend films, their thermal stability and characteristic thermal transitions have been evaluated and the results are reported in **Table 2** and **Figure 4**.

PBCEA, notwithstanding the significant content of aliphatic sequences, shows high thermal stability, due to the presence of cycloaliphatic sub-units. In fact, similarly to PBCE,(Gigli et al., 2016) its degradation occurs in a single step leading to 100% mass loss above 650°C, and the maximum degradation temperature (T_{max}) is registered over 420°C (**Table 2**).

Table 2. Thermal properties of PBCEA and PBCEA/TPS blend films

	TGA				II scan, DSC				Cooling, DSC	
	$T_{onset,I}$ (°C)	$T_{max,I}$ (°C)	$T_{onset,II}$ (°C)	$T_{max,II}$ (°C)	T_g (°C)	ΔC_p ($J°C^{-1}g^{-1}$)	T_m (°C)	ΔH_m (Jg^{-1})	T_c (°C)	ΔH_c ($J\,g^{-1}$)
PBCEA	/	/	405±1	431±2	-17±1	0.08±0.01	139±1	28±1	118±1	-28±1
PBCEA/TPS	326±1	341±1	406±1	437±1	-19±1	0.06±0.01	136±1	18±1	115±1	-19±1
PBCEA/TPS-CA0.5	325±1	340±1	407±2	439±1	-17±1	0.04±0.01	135±1	15±1	113±1	-15±1
PBCEA/TPS-CA1	323±2	341±1	405±1	439±1	-18±1	0.04±0.01	134±1	13±1	113±1	-13±1

On the other hand, the introduction of adipic acid subunits randomly distributed along the poly(butylene cyclohexanedicarboxylate) (PBCE) chains caused significant reduction of the copolymer glass transition and melting temperature, which respectively decreased of 29 and 28°C as compared to PBCE.(Gigli, Lotti, et al., 2014; Gigli et al., 2016) In particular, the lowering of T_m permitted the use of milder conditions for the blend processing, and thus the reduction of the kinetic of unwanted starch degradation reactions.(W.-C. Liu et al., 2010)

The thermal stability profile of the blends, differently from PBCEA, is characterized by three weight loss steps (**Figure 4A**), as previously observed.(Genovese et al., 2018) The first degradation segment, below 150°C, is due to absorbed water evaporation. Then, before the second degradation step, a slight decrease of weight, whose intensity well correlates with the CA content, can be observed in the blends. This phenomenon might be due to the degradation of low molecular weight products generated by the CA-mediated depolymerization action during extrusion. Lastly, the second (T_{onset} = 323 – 326°C) and the third step are respectively related to starch and PBCEA backbone degradation (**Figure 4A**).

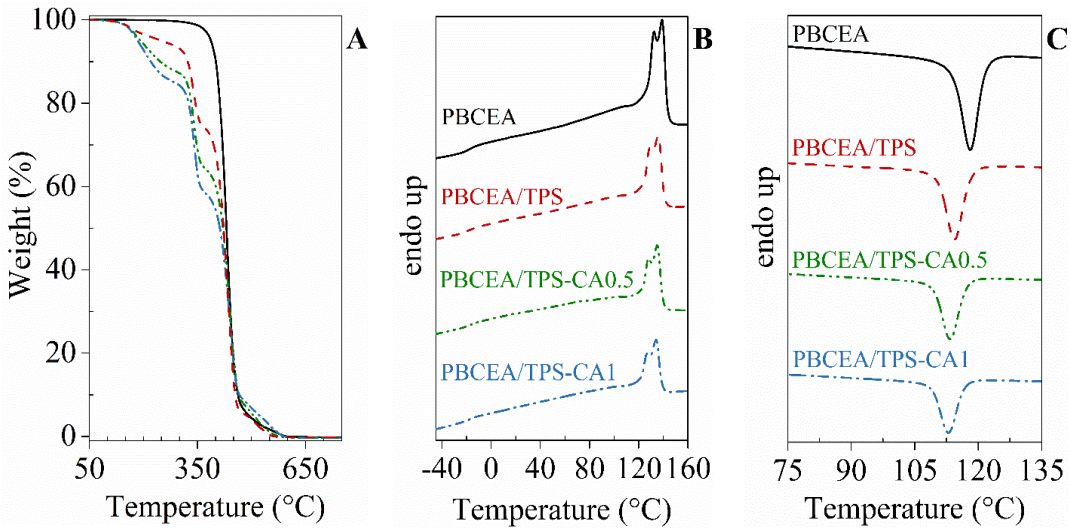

Figure 4. Thermogravimetric curves (A), II scan DSC (B) and crystallization exotherms (C) of PBCEA and PBCEA/TPS blends

The CA addition also impacted the melting behavior of the PBCEA/TPS blends, while glass transition remained unaffected (**Table 2**). Specifically, with the increase of CA load, a progressive decrease of the melting temperature can be observed, indicating an improved dispersion of the TPS into the PBCEA matrix, which in turn hampers the polyester crystals' perfection. (**Figure 4B**). Nevertheless, PBCEA in the blends reaches the same degree of crystallization as in the pristine polymer, as comparable ΔH_m are observed (it must be considered that the blends contain only 50% of PBCEA). These results are further confirmed by analyzing the blends crystallization behavior (**Figure 4C**),

where a lowering of the crystallization temperature is recorded for PBCEA/TPS-CA0.5 and PBCEA/TPS-CA1 samples.

The analysis of surface wettability and moisture content that different formulations can absorb in specific environmental conditions is of great importance for packaging applications. These data acquire even more relevance due to the hydrophilic nature of thermoplastic starch, its brittleness, and high sensitivity to moisture, which limit its uses as packaging material.(Ivanič et al., 2019) **Table 3** summarizes the moisture content (MC) values of the different blends after 1 and 5 storage weeks at 53% RH and 25°C. The MC of neat PBCEA film remained unchanged between 1 and 5 weeks, indicating that equilibrium conditions were already reached in the first week of storage, as described for other thermoplastic polymers.(A. Cano et al., 2016; A. I. Cano et al., 2015; F. Luzi et al., 2018; F. Luzi et al., 2017)

As expected, PBCEA blending with TPS induces an increase of MC, thus confirming what already indicated by ATR-FTIR. This phenomenon is related to the higher affinity of TPS to water with respect to PBCEA. Furthermore, the moisture content is enhanced by higher contents of CA, because of the plasticizing effect of this latter that influences the absorption of humidity,(Ivanič et al., 2019) being however, well below the reported values for CA-plasticized TPS, i.e. above 30%.(Jiugao et al., 2005) Also for the blends, after 5 weeks of storage, the MC data did not drastically vary as compared to those registered after 1 week (**Table 3**). However, while PBCEA/TPS displayed a lowering of the water content, in CA-containing samples the MC either slightly increased or remained constant, meaning that in these latter no significant retrogradation occurred over the monitored time span. Surface wettability data (**Table 3**) are in good agreement with MC and well correlate with the results of the ATR-FTIR analysis. In particular, TPS-containing samples are more hydrophilic than neat PBCEA, as due to a higher amount of hydroxyl groups.

Table 3. Water contact angle (WCA), moisture content and mechanical properties of PBCEA and PBCEA/TPS blends

		Moisture content (% wt.)		**Tensile properties**				
	WCA (°)	**1 week**	**5 weeks**	**E (MPa)**	**σ_y (MPa)**	**ε_y (%)**	**σ_b (MPa)**	**ε_b (%)**
PBCEA	81 ± 1	0.34±0.01	0.34±0.01	227 ± 18	18.6 ± 1.0	27 ± 1	37.7 ± 1.4	800 ± 50
PBCEA/TPS	76 ± 3	1.11±0.08	0.76±0.13	91 ± 8	/	/	12.2 ± 0.6	426 ± 27
PBCEA/TPS-CA0.5	76 ± 4	1.88±0.14	2.21±0.03	84 ± 1	/	/	12.8 ± 0.9	440 ± 40
PBCEA/TPS-CA1	70 ± 4	2.28±0.08	2.16±0.06	60 ± 7	/	/	12.7 ± 0.8	478 ± 16

Even if TPS tensile characteristics can vary depending on the starch' source, its physicochemical properties, e.g. degree of crystallinity and T_g, and used plasticizer, it is not suited for high-

performance applications, as it displays very low tensile strength, of about 2-6 MPa, and elongation at break (ε_b) generally below 60-70%.(Cyras et al., 2008; Zhang et al., 2014) To verify if the blending with PBCEA resulted in improved mechanical behavior, tensile tests have been carried out on the prepared PBCEA/TPS blends. Representative stress-strain curves are reported in **Figure 5** and the results are contained in **Table 3**. PBCEA shows a typical hard and tough plastic behavior, with clearly visible yield and high elongation at break (**Table 3**). Therefore, with respect to PBCE homopolymer, for which ε_b equal to 30% and elastic modulus (E) of ca. 460 MPa have been described,(Gigli et al., 2013, 2016; Gigli, Govoni, et al., 2014) the introduction of flexible aliphatic co-units significantly modified its behavior, as E value halved and ε_b increased more than 26 times. Subsequent blending with TPS caused a further substantial variation of the tensile features of PBCEA, as the blends' behavior resemble that of elastomers. In fact, the yield point is not visible and a substantial drop of E (up to 4× lower for PBCEA/TPS-CA1), that gradually decreases with the increase of CA concentration due to the lower amount of crystalline domains (**Table 2**), can be observed. Elongation at break is lower than neat PBCEA, but higher than 400% in all cases, testifying the good compatibility among the blend components. A slight dependence on the CA concentration can be observed, too. Interestingly, the micro-porosity in the CA-containing samples does not compromise their tensile characteristics, as comparable stress at break and improved deformability with respect to the CA-free blend have been measured.

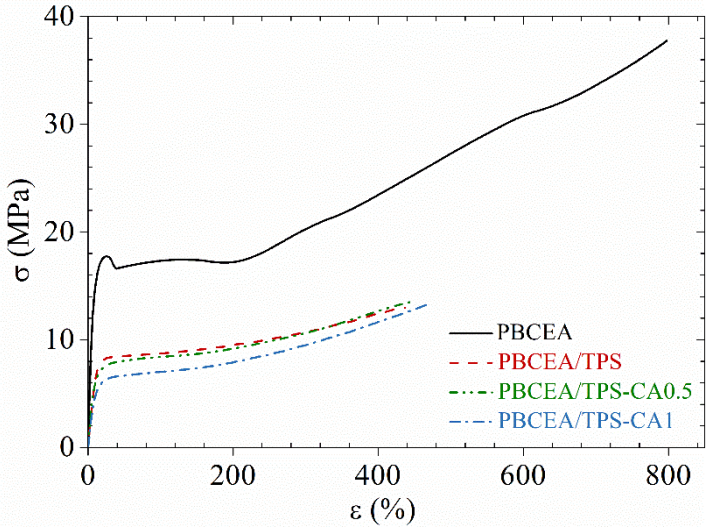

Figure 5. Representative stress-strain curves of PBCEA and PBCEA/TPS blends

These data acquire more value if compared to those of PBAT/TPS blend films recently reported.(Fourati et al., 2018) In this case, the addition of various concentrations of CA to 40/60 blends caused a significant worsening of the performances, as the strength decreased from 10.2 to ca. 3 MPa and ε_b declined from almost 200% to a maximum of 37%.

Last, but not least, the end of life fate of the PBCEA/TPS blends has been investigated through a lab-scale composting test carried out over a 4 months' timeframe. Weight loss values (**Figure 6**) evidence a clear dependence on the blend composition. Firstly, it can be observed that PBCEA does not undergo any degradation in the time scale explored, and both film surface and cross section seem to be unaffected by the incubation in compost (**Figure 7**). The result is not surprising because it was previously demonstrated that substantial chemical modification of PBCE-based polyesters, e.g. by the insertion of polar groups along the polymer backbone, is necessary to speed-up the biodegradation process.(Genovese et al., 2016; Gigli, Lotti, et al., 2014)

Once again, the blending with 50% of TPS induced a significant change in the degradation kinetics of the samples, which resulted further related to the CA content. In particular, the weight losses of the blends are characterized by two well-distinct regions. In the first 30 – 40 days of incubation a rapid increase of the weight loss has been observed, then followed by a flat trend. In the second part of the experiment, no additional weight losses have been indeed recorded. Furthermore, while PBCEA/TPS only reached about 15% loss, for both PBCEA/TPS-CA0.5 and PBCEA/TPS-CA1 values around 45%, almost equivalent to the whole TPS content, have been reached. However, some differences can be highlighted, as the sample with a higher CA loading showed a much faster kinetic of degradation. The results clearly indicate that TPS is much more easily degraded in CA containing samples. This observation supports the above mentioned hypothesis that CA not only favors transesterification reactions, thus improving blend compatibility, but also catalyzes TPS hydrolysis during the extrusion process, which consequently facilitates the degradation process during composting.(Carvalho et al., 2005) The higher the CA content, the greater the depolymerization action on TPS, thus the faster the weight losses.

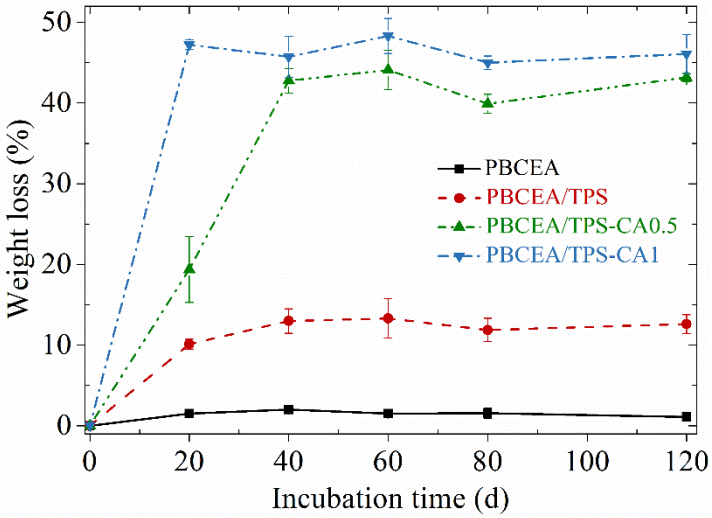

Figure 6. Gravimetric weight loss of PBCEA and PBCEA/TPS blends as a function of composting time

SEM micrographs on partially degraded samples (**Figure 6**) confirmed the described trend. In fact, both surface and cross section of PBCEA/TPS based blends appeared significantly affected by the enzyme action.

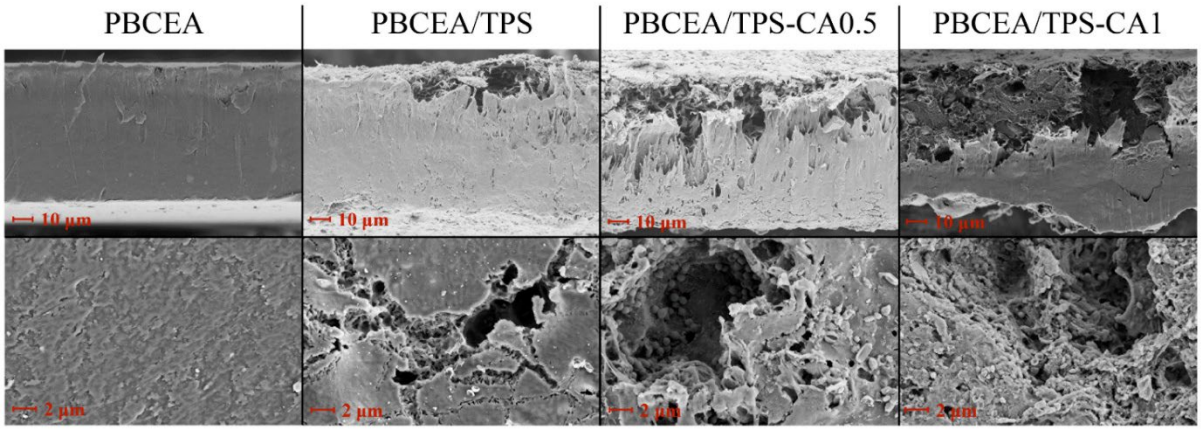

Figure 7. FESEM micrographs of PBCEA and PBCEA/TPS blends after 120 d of incubation in compost (top: cross section, bottom: film surface)

Cavities as big as a few microns, whose size and amount increases with the CA % wt., are fully visible on the film surface. These holes deeply penetrate into the film thickness, reaching a depth of about 30 µm in PBCEA/TPS-CA1. The additional presence of micro-porosities may have exerted a positive role in the process, by exposing a higher surface area to the enzymatic attack.

4. Conclusions

Films of PBCEA/TPS blends, containing a variable amount of citric acid, have been successfully prepared. All components of the formulation contributed to the achievement of a novel ecofriendly material with fully bio-based character, high flexibility, good moisture resistance and fast degradability in compost.

Specifically, the introduction along the PBCE backbone of a specific amount of adipate co-units revealed a winning strategy to modulate the melting temperature of the polyester matrix and enhance the film flexibility, while maintaining sufficient crystallization ability and very good thermal stability. In particular, the decrease of T_m allowed for the adoption of milder conditions during the melt blending process, thus limiting the occurrence of unwanted starch degradation reactions.

In addition, the presence of CA had two positive effects: 1) compatibilization, through crosslinking and (trans)esterification reactions, was confirmed by SEM analysis, which evidenced a better interfacial adhesion between the two blend components, and by calorimetric studies that highlighted a reduction of the crystallization ability of the PBCEA domains; 2) formation of micro-porosities, due hydrolysis reactions, that, by increasing surface area, accelerated the water- and enzyme-

mediated fragmentation process under composting conditions, without having any detrimental effect on the mechanical characteristics.

CRediT authorship contribution statement

F.Dominici: conceptualization, methodology; M.Gigli: conceptualization, methodology, data curation, writing – original draft, review and editing; I.Armentano: investigation, validation, writing – original draft; L.Genovese: investigation; F.Luzi: validation, resources; L.Torre: review; A.Munari: resources, supervision; N.Lotti: conceptualization, supervision, writing - review and editing, project administration.

Conflict of interest

The authors declare no conflict of interest.

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